Gas Phase Reactions of Protonated 1,3-Diphenylpropyne and Some Isomeric \([\text{C}_{15}\text{H}_{13}]^+\) Ions

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Metastable (3-phenyl-2-propyny1)benzenium ions, generated by electron impact induced fragmentation from the appropriately substituted 1,1-dihydrobenzoic acid, react by loss of \('\text{CH}_3\) and \('\text{C}_6\text{H}_4\). The study of deuterated derivatives reveals that hydrogen/deuterium exchanges involving all hydrogen and deuterium atoms precede the fragmentations. The results suggest a skeletal rearrangement by electrophilic ring-closure reactions giving rise to protonated phenylindene and protonated 9,10-methano-9,10-dihydroanthracene prior to the elimination of \('\text{C}_6\text{H}_4\) and \('\text{CH}_3\), respectively. A study of isomeric \([\text{C}_{15}\text{H}_{13}]^+\) ions by collision-induced decomposition and by deuterium labelling shows that these ions interconvert by hydrogen migrations and skeletal rearrangements.

Previous studies\(^1,\)\(^2\) have shown that a fast interannular proton transfer occurs in ring-protonated \(\alpha,\omega\)-diphenylalkanes \(a\) which can be generated in a mass spectrometer by chemical ionization (CI) of \(\alpha,\omega\)-diphenylalkanes \(1\) (Scheme 1, route a) and by electron impact (EI) induced fragmentation of \(\omega\)-phenylalkyl-1,4-dihydrobenzoic acids \(2\) (Scheme 1, route b), respectively. This proton transfer between both phenyl groups can be detected by the elimination of the isotopomers of benzene from metastable ions\(^3\) in the first field-free region (1st FFR) and the second field-free region (2nd FFR) of a VG ZAB-2F mass spectrometer using compounds specifically labelled on one of the phenyl groups.

Similar steric effects are expected for the proton exchange reactions of protonated 1,4-diphenylbutyne and protonated 1,3-diphenylpropyne in which the two phenyl groups are kept apart by the alkynyl groups. However, the mass spectrometric reactions, especially of (3-phenyl-2-propynyl)benzenium ions \(b\), show effects which must be due to skeletal rearrangements in addition to proton exchange reactions. Here, we report the results of a study of these reactions of \([\text{C}_{15}\text{H}_{13}]^+\) ions.

RESULTS AND DISCUSSION

(3-Phenyl-2-propynyl)benzenium ions \(b\), of m/z 193 and specifically protonated at one of the phenyl groups, arise in the EI mass spectrum (see Fig. 1) of 1-(3-phenyl-2-propynyl)-1,4-dihydrobenzoic acid \(3\) and specifically protonated at one of the phenyl groups, in the EI mass spectrum (see Fig. 1) of 1-(3-phenyl-2-propynyl)-1,4-dihydrobenzoic acid \(3\) by loss of the \('\text{COOH}\) radical. The EI-induced decomposition of this compound as deduced from an investigation of metastable ions is shown in Scheme 2. In contrast to the 70 eV EI mass spectrum, the abundances of the ions m/z 116 and m/z 115 are very small in the mass-analysed ion kinetic energy (MIKE) spectrum\(^4\) of the molecular ions of \(3\). The main reaction path of the metastable molecular ions is the loss of \('\text{COOH}\) and the formation of (3-phenyl-2-propynyl)benzenium ions \(b\).

The MIKE spectrum of ions \(b\) (Fig. 2) shows peaks for the loss of \('\text{H}\) (m/z 192), \('\text{CH}_3\) (m/z 178), \('\text{C}_6\text{H}_4/\text{C}_7\text{H}_3\) (m/z 165/164) and \('\text{C}_6\text{H}_6\) (m/z 115) from metastable ions in the 2nd FFR. The same reactions occur with similar relative rates in the 1st FFR as shown by a B/E linked-scan spectrum\(^5\) of ions \(b\). The deuterated ions \(b_1\) and \(b_2\), specifically labelled at the original phenyl group and at the methylene group of

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the carbon bridge, respectively (Scheme 3), lose all possible isotopomers of methyl and benzene in the 1st FFR and 2nd FFR. However, while these results indicate extensive H/D exchange reactions in metastable $b_1$ and $b_2$ ions the data of Table 1 show clearly that complete scrambling over all positions at the phenyl groups or of all hydrogen atoms does not take place.

The reactions of metastable (3-phenyl-2-propynyl)benzenium ions $b$ differ from those of $\omega$-phenylalkylbenzenium ions (a)$^{1,2}$ in three aspects: (i) Elimination of a $C_6H_6$ molecule dominates the fragmentation of ions $a$ while ions $b$ lose preferentially a $'CH_3$ radical. (ii) The hydrogen migrations occur in ions $a$ only between the two rings whereas in ions $b$ the hydrogen atoms of the bridge also participate in the hydrogen exchange. (iii) In contrast to ions $a$ the hydrogen exchange in ions $b$ does not result in a statistical distribution of the label over all ring-positions.

Nevertheless, the data of Table 1 prove that both phenyl groups have become equivalent prior to the elimination of benzene. These results clearly indicate other rearrangement reactions besides hydrogen migration and can be accounted for by the reaction sequences shown in Schemes 4 and 5.

The first step in the rearrangement of ion $b$ is a proton transfer to the central carbon atom (C(2))
Table 1. Relative abundances for the loss of isotopomers of benzene and methyl radical from metastable ions $b_1$ and $b_2$

<table>
<thead>
<tr>
<th>Ion</th>
<th>$1^\text{st}$ FFR</th>
<th>$2^\text{nd}$ FFR</th>
<th>Calc. for $6\text{H}/5\text{D}$</th>
<th>Calc. for $8\text{H}/5\text{D}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$-\text{C}_6\text{H}_6$</td>
<td>$-\text{C}_6\text{H}_5\text{D}$</td>
<td>$-\text{C}_6\text{H}_5\text{O}_2$</td>
<td>$-\text{C}_6\text{H}_5\text{D}_2$</td>
</tr>
<tr>
<td>$b_1$ 1st FFR</td>
<td>15</td>
<td>21</td>
<td>18</td>
<td>16</td>
</tr>
<tr>
<td>$b_1$ 2nd FFR</td>
<td>12</td>
<td>19</td>
<td>17</td>
<td>16</td>
</tr>
<tr>
<td>Calc. for $6\text{H}/5\text{D}$</td>
<td>0.2</td>
<td>6.5</td>
<td>32.5</td>
<td>43.3</td>
</tr>
<tr>
<td>Calc. for $8\text{H}/5\text{D}$</td>
<td>1.3</td>
<td>16.3</td>
<td>40.8</td>
<td>32.6</td>
</tr>
<tr>
<td>$b_2$ 1st FFR</td>
<td>53</td>
<td>33</td>
<td>14</td>
<td>—</td>
</tr>
<tr>
<td>$b_2$ 2nd FFR</td>
<td>54</td>
<td>38</td>
<td>8</td>
<td>—</td>
</tr>
<tr>
<td>Calc. for $11\text{H}/2\text{D}$</td>
<td>26.9</td>
<td>53.9</td>
<td>19.2</td>
<td>—</td>
</tr>
</tbody>
</table>

which is the most basic position of the hydrocarbon.\(^6\)

Formations of $c$ from $b$ is exothermic by about 69 kJ mol\(^{-1}\) (see Table 2 for the estimated heats of formation of relevant \(\text{[C}_{15}\text{H}_{13}]^+\)) ions). Electrophilic attack of the vinyl ion on the phenyl group\(^7\) generates a protonated phenylindene ion $d$ in which migration of the proton gives rise to $d',d''$ and other isomers prior to loss of a benzene molecule and formation of an indenyl ion $e$.\(^8,9\) A second intramolecular electrophilic substitution of the 3-phenylindanyl ion $d^*$ leads to a protonated 9,10-methano-9,10-dihydro-anthracene ion $f$ which decomposes to ionized anthracene $g$ by loss of a methyl radical. Hence, the competition between loss of $\text{C}_6\text{H}_6$ and loss of $\text{CH}_3$ from metastable ions $b$ can be explained by the formation of the stable product ions $e$ and $g$. The heats of formation of the key intermediates of both fragmentation reactions, i.e. the protonated phenylindenones $d-d^*$ and the protonated 9,10-methano-9,10-dihydro-anthracene $f$, respectively, are below that of the educt ion $b$ (Table 2) so that these intermediate ions are formed with excess energy, facilitating hydrogen exchange reactions via ions $d-d^*$. A preceding hydrogen migration within the vinyl ion $c$ gives rise to the 1,3-diphenylallyl ion $i$ in which both phenyl groups are in equivalent positions because of the resonance structures\(^1\) (\(i\leftrightarrow i',\) Scheme 5). Thus, this hydrogen migration makes the phenyl groups equivalent prior to the ring closure to ion $d$. A second mechanism which equilibrates the phenyl groups after the ring-closure reaction consists of the hydrogen migration $d \rightarrow d''$ (Scheme 5) and the ring-opening/ring-closure reaction $d'' \rightarrow d''$, via the 1,1-diphenylallyl ion $j$. A similar mechanism has been proposed for a phenyl migration in the phenyl-2-azaallyl cation.\(^9\)

The validity of the rearrangement reactions of \(\text{[C}_{15}\text{H}_{13}]^+\) ions suggested in Schemes 4 and 5 can be tested by generating the various isomeric \(\text{[C}_{15}\text{H}_{13}]^+\) ions independently. Assuming no isomerization prior to the fragmentations, the ions $c, d^*, h$ and $i$ are formed by the electron impact induced fragmentations shown in Scheme 6 from the precursors 4–7. Similarly, protonation of 8 and 9 in a chemical ionization experiment gives rise to ions $d^+$ and $f$ or their tautomers, respectively. The MIKE spectra of \(\text{[C}_{15}\text{H}_{13}]^+\) ions generated by the reactions of Scheme 6 contain signals due to the losses of $'\text{H}$, $'\text{CH}$, and $'\text{C}_6\text{H}_6$ which have also been observed for metastable ions $b$ (Table 3).

Thus, all metastable \(\text{[C}_{15}\text{H}_{13}]^+\) ions decompose by the same fragmentations. However, the relative abundances of the resulting fragment ions are different, and most of the \(\text{[C}_{15}\text{H}_{13}]^+\) ions eliminate more $'\text{C}_6\text{H}_6$ than does $b$. This can be attributed to differences in the excess energy of the \(\text{[C}_{15}\text{H}_{13}]^+\) ions of different origins. The effect of different excess energies is clearly indicated by the different MIKE spectra of ions $d^*$ and $d^+$ which have been generated by electron impact induced fragmentation of 7 and by gas phase
Table 2. Estimated heats of formation, ΔHf, of ions given in Schemes 4 and 5

<table>
<thead>
<tr>
<th>Ion</th>
<th>ΔHf (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>b</td>
<td>1139a</td>
</tr>
<tr>
<td>c</td>
<td>1070b</td>
</tr>
<tr>
<td>d*</td>
<td>~970b</td>
</tr>
<tr>
<td>d+</td>
<td>959b</td>
</tr>
<tr>
<td>e</td>
<td>1000.10a</td>
</tr>
<tr>
<td>f</td>
<td>~960a</td>
</tr>
<tr>
<td>g</td>
<td>954c</td>
</tr>
<tr>
<td>h</td>
<td>1133h</td>
</tr>
<tr>
<td>i</td>
<td>&lt;1056i</td>
</tr>
</tbody>
</table>

* And tautomers.

From ΔHf(C₆H₄CH₂C≡CCH₃) = 426 kJ mol⁻¹ (by increments³⁶) and PA(C₆H₄CH₂C≡CCH₃) = 815 kJ mol⁻¹,³⁷b

* By isodesmic reaction using ΔHf(C₆H₄CH₂C≡CCH₃) = 327 kJ mol⁻¹,¹⁰d, ΔHf(C₆H₄C≡CCH₃ = CH₂) = 971 kJ mol⁻¹,¹⁰b, and ΔHf(C₆H₆C≡CCH₃) = 426 kJ mol⁻¹,¹⁰a

* From ΔHf(3-phenylindene) = 256 kJ mol⁻¹ (by increments¹⁰b), and PA(3-phenylindene) = PA(o-xylene) = 817 kJ mol⁻¹,³⁸b

* By isodesmic reaction using ΔHf(C₆H₄CH = CH₂) = 147 kJ mol⁻¹,¹⁰a, ΔHf(C₆H₄CH₂CH = CH₂) = 837 kJ mol⁻¹,¹⁰d, and ΔHf(1-phenylindene) = 269 kJ mol⁻¹ (by increments¹⁰a).

With ΔHf(C₆H₆) = 83 kJ mol⁻¹,¹⁰e and ΔHf(CH₃) = 142 kJ mol⁻¹,¹⁰a, the combined ΔHf of the fragmentation products are (a + C₆H₆) = 1083 kJ mol⁻¹ and (g + CH₃) = 1056 kJ mol⁻¹, respectively.

From ΔHf(9,10-methano-9,10-dihydroanthracene) = 249 kJ mol⁻¹ (by increments¹⁰b) and PA(o-xylene) = 817 kJ mol⁻¹,³⁸b

* By isodesmic reaction using ΔHf(CH₃CH = CH₂) = 913 kJ mol⁻¹,¹⁰b, ΔHf(C₆H₄CH₂CH = CH₂) = 50 kJ mol⁻¹,¹⁰d, ΔHf(C₆H₄CH = CH₂) = 52 kJ mol⁻¹,¹⁰d, ΔHf(C₆H₄CH₂CH = CH₂) = 147 kJ mol⁻¹,¹⁰d, and ΔHf(CH₃) = 75 kJ mol⁻¹,¹⁰d.

* By isodesmic reaction using ΔHf(C₆H₄CH₂CH = CH₂) = 837 kJ mol⁻¹,¹⁰d, ΔHf(C₆H₄CH = CH₂) = 147 kJ mol⁻¹,¹⁰d, and ΔHf(CH₃) = -75 kJ mol⁻¹,¹⁰d. The calculated value is an upper limit because of an additional stabilization by the vinyl group.

The protonation of 8, respectively (Scheme 6). Ions d* and d⁺ interconvert by allowed hydride shifts and, hence, would be expected to give the same MIKE spectra. Similarly, the vinyl ions c and h interconvert by an allowed 1,2-hydride shift, but in spite of the expected equilibration between both structures the MIKE spectra of c and h are different (Table 3).

In agreement with this explanation the peak pattern produced by collisional induced decomposition (CID) of metastable [C₁₅H₁₃]+ ions c, d*, d⁺, f, h and i (Scheme 6) in the CID/MIKE spectra are identical within the limits of error (Table 4).†

Although this result indicates an interconversion of the isomeric [C₁₅H₁₃]+ ions c, d*, d⁺, f, h and i (Scheme 6) in the CID/MIKE spectra are identical within the limits of error (Table 4).†

Although this result indicates an interconversion of the isomeric [C₁₅H₁₃]+ ions according to the Schemes 4 and 5 after collisional activation, the isomerization reactions are obviously slow processes in metastable [C₁₅H₁₃]+ ions because the H/D exchanges in the deuterated b₁ and b₂ ions have not reached the statistical distribution (Table 1). A similar effect is observed in the MIKE spectra of the deuterated vinyl ions c₁ and allyl ions i₁ (Scheme 6). Again the elimination of all isotopomers of methyl and benzene occurs, but the intensity distribution observed for the reactions of metastable ions in the 2nd FFR is far from the statistical values (Table 5).

It is of interest to note that the distribution of deuterium label in the reaction products of metastable ions b₁ (Table 1) is identical, but different from that of metastable ions b₁ (Table 5). A rapid equilibration c ⇌ h ⇌ i (Scheme 5) puts both phenyl groups into identical positions. The subsequent reaction via ring closure to ions d and d⁺ followed by elimination

Table 3. MIKE spectra of some [C₁₅H₁₃]+ ions (Scheme 6)

<table>
<thead>
<tr>
<th>Ion</th>
<th>-H'</th>
<th>-CH₃</th>
<th>-C₆H₆</th>
</tr>
</thead>
<tbody>
<tr>
<td>b</td>
<td>29</td>
<td>57</td>
<td>14</td>
</tr>
<tr>
<td>c</td>
<td>22</td>
<td>33</td>
<td>45</td>
</tr>
<tr>
<td>d*</td>
<td>24</td>
<td>47</td>
<td>29</td>
</tr>
<tr>
<td>d⁺</td>
<td>30</td>
<td>56</td>
<td>14</td>
</tr>
<tr>
<td>f</td>
<td>25</td>
<td>50</td>
<td>25</td>
</tr>
<tr>
<td>h</td>
<td>17</td>
<td>33</td>
<td>50</td>
</tr>
<tr>
<td>i</td>
<td>42</td>
<td>26</td>
<td>32</td>
</tr>
</tbody>
</table>

† The loss of CH₃ and C₆H₆ from metastable [C₁₅H₁₃]+ ions also occurs by CID which can be separated from the corresponding unimolecular reactions by applying a voltage to the collision cell. The intensity ratio -CH₃/-C₆H₆ for the CID process is constant for ions h, c, d*, d⁺, f, h and i, in contrast to the behaviour of these ions during unimolecular fragmentations (Table 3).
of a benzene molecule without additional hydrogen migrations in the intermediate ions gives rise to the loss of C₆H₄D and C₆HD₅, respectively. This corresponds to the maxima of the intensity distribution for benzene elimination from metastable b₁, c₁ and i₁, but the distribution is more peaked for the latter two ions. This result shows that the isomerization c→h→i by 1,2-hydride shifts is fast, and that there is less excess energy available for hydrogen migrations in the ions c(c₁) and i(i₁) formed by EI-induced fragmentation from the halides 4(4a) and 6(6a) than in those ions formed by an exothermic hydrogen migration from ions b(b₁). The same conclusion follows from an analysis of the intensity distribution for the loss of the isotopomers of the methyl group. The formation of f (Scheme 4) from an equilibrium mixture c→h→i via d and d* without much hydrogen migration between both aromatic groups would result mainly in the loss of CH₂D in the case of the pentadeuterated ions which, indeed, is observed for the fragmentation of metastable ions c₁ and i₁. Therefore, the hydrogen migrations between the aromatic moieties of the protonated 1-phenylindene ions d→d* are slow compared to further fragmentations. This result is corroborated by the observation of a slow H/D exchange in protonated pentadeuterodiphenylmethane ions, in contrast to the behaviour of the higher homologues of the \( \omega \)-phenylalkylbenzenium ions.

**EXPERIMENTAL**

**Mass spectrometry**

The mass spectrometric measurements were performed with a double focusing mass spectrometer VG-ZAB-2F equipped with a combined EI/CI ion source using the following experimental conditions:

**EI** Electron energy, 70 eV; electron trap current, 50 μA; ion source temperature, c. 180 °C, accelerating voltage, 6 kV.

**CI** Reagent gas, CH₃; electron energy, 100 eV; electron emission current, 100 μA, ion source temperature, c. 180 °C, accelerating voltage, 6 kV.

The reactions of metastable ions in the 1st FFX and 2nd FFR of this instrument were studied in the usual manner. CID/MIKE spectra were obtained by introducing He into the collision chamber of the 2nd FFR.

**Synthesis of compounds**

1-[(3-Phenyl-2-propyn)-1,4-dihydrobenzoic acid (3). 3-Phenyl-2-propynyl bromide (b.p. 115–117 °C/12 Torr) was obtained in 48% yield from the corresponding alcohol by reaction with Br₂/(C₆H₅)₂P in CCl₄. The reductive alkylation of benzoic acid by this bromide in liquid NH₃ yields 3. M.p.: 115–116 °C; \(^{1}H\)-NMR (CDCl₃): δ 10.68 (s, 1H), δ 7.17–7.35 (m, 5H), δ 5.94 (s, 2H), δ 2.80 (s, 2H), δ 2.69 (t, 2H).

**Deuterated 1-[(3-phenyl-2-propyn)-1,4-dihydrobenzoic acids (3a and 3b). The deuterated dihydrobenzoic acids 3a and 3b were synthesized by the same procedures as 3 using the appropriately labelled bromides. These bromides were obtained from the corresponding propinols. 3-Phenyl-d₅-2-propyn-1-ol was prepared as follows: Phenyl-d₅-ethin was prepared from benzaldehyde-d₅ by a Wittig reaction with \((\text{C}_6\text{H}_5)_3\text{PCH}_3\text{Br}^–\) and addition of Br₂ to the resulting styrene-d₅ followed by base-catalysed elimination of HBr. Reaction of phenyl-d₅-ethin with EtMgBr followed by addition of CH₂O resulted in the 3-phenyl-d₅-2-propyn-1-ol in a total yield of 19%. \(^{1}H\)-NMR...
showed no signals due to $^1$H at the phenyl group. 3-Phenyl-2-propin-1-ol-1-d$_2$ was obtained from phenylpropionic acid methyl ester by reduction with LiAID$_4$ in ether (80%).

1-Chloro-1,3-diphenyl-1-propene (4), 3-bromo-1,3-diphenyl-1-propene (6)\textsuperscript{15} and 9,10-dihydro-9,4-methanoadanthracene (9)\textsuperscript{16} were obtained as described in the literature. The corresponding phenyl-d$_2$-derivatives 4a and 6a were prepared by using C$_6$D$_5$MgBr during the synthesis.

2-Chloro-1,3-diphenyl-1-propene (5) (b.p. 134°C/0.1 Torr) was obtained by reaction of PCl$_3$ with 1,3-diphenylacetone in benzene in 33% yield.

Acknowledgement

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